

MULTIPLE CAGE OCCUPANCY AND CRYSTAL STRUCTURE VARIATIONS IN NATURAL GAS CLATHRATE HYDRATES

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ABSTRACT

New experimental setup for neutron diffraction at high hydrostatic pressure (up to 10kbar) and in the 10-300 K temperature range was developed at Los Alamos Neutron Science Center, LANL. The crystal structure transformations and the phase diagrams were determined for the $H_2(D_2)$, N_2 , Ne, Ar, Kr and Xe clathrate hydrates as a function of temperature and pressure. At ambient pressure multiple guests' occupancies in the cages were found for H_2 and Ne clathrates. Hydrogen occupancy in the $(32+X)H_2 \cdot 136H_2O$, $x=0-16$ clathrate varies by changing the large (hexakaidecahedral) cage occupancy between 2 and 4 molecules, but keeping single occupancy of the small (dodecahedral) cage in the sII structure. Neon clathrate also crystallizes in the sII but has the fixed composition of $32Ne \cdot 136H_2O$ corresponding to singly occupied dodecahedral cage and double occupancy in the hexakaidecahedral cage. Under high pressure N_2 , Ar and Kr clathrate hydrates form different structures including ones with multiply occupied cages. Localization- delocalization of the guest molecules in the multiply occupied cages was investigated by Rietveld analysis, using special form-factors and spherical harmonic expansion for the nuclear density. The guest-host interaction plays an important role in the clathrate structure formation and stability.

Keywords: hydrogen clathrate, multiple cage occupancy

INTRODUCTION

Clathrate hydrates represent a class of inclusion compounds, with the host framework made up of hydrogen bonded H_2O molecules, and guest molecules trapped inside the framework cages. Gas hydrates is a large subgroup of clathrate hydrates forming mostly under high pressure or/and low temperatures. Hydrates of natural gases prevail in deep-sea sediments and permafrost, and could play an important role in the formation of the planetary nebulae [1-5]. Earlier studies of the clathrate crystal structures by X-ray and neutron diffraction revealed a variety of structure types, differing by

type and arrangement of polyhedral cages. The cages occupancy by gas molecules found to be variable but the maximum guest/ H_2O molar ratios have been determined around 0.16, corresponding to the single occupancy of each cage (Villard's rule) [1].

However, huge disproportions between the sizes of some molecules and the cages dimensions allow the assumption that clathrates of small molecules like H_2 , Ne, N_2 , O_2 may have a multiple occupancies of the cages [6,7]. Recently, theoretical calculations [8,9] and Raman studies [10] of the gas hydrates under high pressure in the diamond anvil cells (DAC) confirmed multiple cage occupancies for H_2 , N_2 and O_2 hydrates. Partial double occupancy (< 1.3) of the

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large cage was recognized in the neutron diffraction studies under high pressure for the N_2 and O_2 clathrates as well [11,12]. However, no detailed information on the number and distribution of the guest molecules in the cages were obtained for this group of clathrate hydrates so far.

RESULTS AND DISCUSSION

We performed *in-situ* synthesis and characterization of clathrates with a specially prepared setup for high-pressure and low-temperature neutron diffraction [13]. The general view and the enlarged section view of the setup are shown in Fig. 1. The distinctive feature of the HIPPO diffractometer is its 3 dimensional geometry. It has 6 detector rings, orthogonal to the beam direction and covering the most of the scattering area. We took advantage of this geometry placing the high-pressure cell horizontally, thus, the data collection from a sample is possible with the entire detectors without contamination by the impurity Bragg reflections from the sample surrounding.

Another advantage of the setup is very high intensity of the HIPPO diffractometer and a large sample volume (up to 10 cm^3) of the high pressure cell. All that allows a precise structure analysis with the use of Rietveld and PDF methods, study of equation of states and phase transformations and time resolved structure and kinetics studies with the very short data collection time (about 1 min). The high efficiency of the setup was proven in our study of the crystal structures and kinetics of

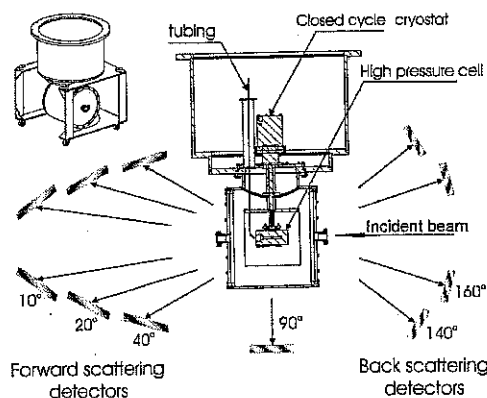


Fig. 1. Schematic general view (in the top left corner) and the enlarged section view of the setup designed for high hydrostatic pressure and low-temperature neutron diffraction experiments at HIPPO diffractometer.

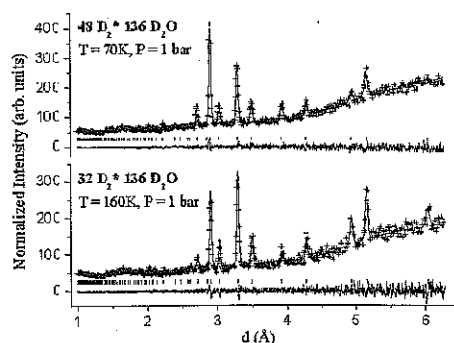


Fig. 2. Rietveld refinement patterns of the neutron diffraction data obtained for deuterium clathrate hydrate with the maximum (top) and minimum (bottom) guest occupancy. The observed intensities are represented by plus signs (every third point is shown), the calculated pattern - by solid line, allowed Bragg positions - by short vertical bars and the difference curve is shown below.

clathrate hydrates under pressures up to 10 kbar and temperatures from 4 to 300 K.

In order to minimize the background of the collected diffraction patterns, deuterated water and D_2 gas (instead of hydrogen analogues) were used for the study of hydrogen clathrate. Synthesis of the clathrate was performed under 2.2 kbar of D_2 pressure at 200-270 K. Neutron diffraction data were collected at 40-300 K under varying pressures and were used for the crystal structure refinement by the Rietveld method Fig. 2 [14]. Over the entire temperature range studied the deuterium clathrate was found to crystallize in $Fd\bar{3}m$ space group with a unit cell parameter $a \sim 17\text{ Å}$, known as the clathrate cubic structure II. The framework of this structure consists of two types of cages formed by hydrogen-bonded D_2O molecules. The unit cell contains 8 hexakaidecahedral (6^45^{12}) cages (subsequently referred to as "large") and 16 dodecahedral (5^{12} ; "small") cages.

We found that the number of D_2 molecules and their distribution in the clathrate structure depend on temperature and pressure (Fig. 3 and 4). Below 50 K the guest D_2 scattering density distribution is consistent with the model of localized hydrogen molecules in the framework, which was determined by interpretation of difference Fourier maps. The D_2 molecular scattering factor was calculated assuming a spherical distribution of nuclear density around the molecular centre with a fixed radius of 0.37 Å . The large cage was found to be occupied by four tetrahedrally arranged D_2 molecules

located at 2.93(1) Å from each other and at a distance of 1.80(1) Å from the center of the cage. Each D₂ molecule is oriented toward the centers of hexagons formed by the framework oxygen atoms. A maximum occupancy of only one D₂ molecule was determined in the small cage. The scattering density of this D₂ molecule was refined as statistically distributed between 20 positions oriented towards the oxygen atoms forming the dodecahedral cage. For both cages the refined O-D₂ distance is 3.34(4) Å.

As the temperature increases, D₂ molecules are deintercalated from the large cage, starting at about 70 K under ambient pressure and at 180 K under 2 kbar. The lowest occupancy of the large cage was found to be two, which is probably a minimum value necessary for the stability of the framework structure. The occupancy of the small cage is constant at one D₂ molecule nearly to up the decomposition temperature of ~163(2) K (Fig. 3). This observation reflects the instability of the structure with empty small cages, which occurs locally for the small cage occupancy of less than one D₂ molecule. Accordingly, the hydrogen occupancy in the clathrate is limited by the stoichiometry 48H₂*136H₂O. In contrast, previous experimental results [15] and theoretical calculations [16] suggested a higher H₂/H₂O molar ratio of 0.5 with double occupancy of the small cage. Our new data indicate that the D₂-D₂ and D₂-O interatomic distances do not allow double occupancy of the small cage without a significant compression of the molecules (about 14-19%). Increasing temperature resulted in a change of the distribution of D₂ molecules in both cages as well.

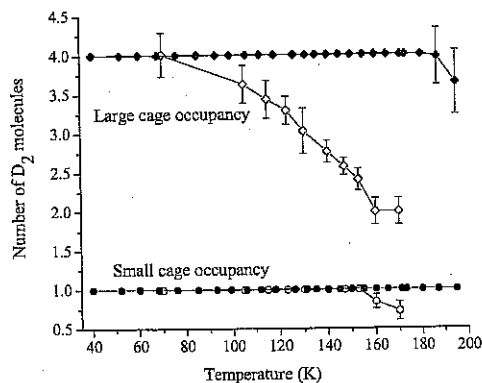


Fig. 3. Temperature dependence of D₂ occupancy in the large (diamond symbols) and small (circle symbols) cages of the hydrogen clathrate hydrate structure. Open symbols represent data obtained at ambient and filled symbols represent data under high pressure (2 kbar).

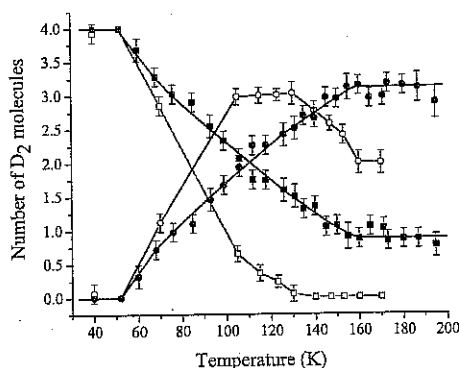


Fig. 4. Temperature dependence of the number of D₂ molecules in the large cage, refined as localized in a tetrahedral cluster (square symbols) and spherically delocalized (circle symbols). Open and filled symbols represent data obtained at ambient and ~2 kbar pressures, respectively. Lines are guides to the eye. At high pressure below ~180 K the total cages occupancy is constant to 4, while at ambient pressure it varies between 2 and 4, that cause the difference in the localization/delocalization behavior.

Successful refinement of the data obtained above 50 K could only be achieved by treatment of the delocalized scattering density as a uniform distribution of the D₂ molecule on the surface of a sphere (rotator model) [17], with a refinable radius and the centre located at the geometric centre of the cavity. In the small cage the "pure" rotator model (without a localized contribution) is preferable for all data obtained above 50 K. In the large cage the total guest D₂ density at intermediate temperatures 60-200 K was approximated by a linear combination of spherically delocalized and localized contributions, and their fractions were refined. Fig. 4 shows a variation of these fractions with temperature at ambient pressure and under 2 kbar. At ambient pressure the onset of the localization of the D₂ molecules coincides with the insertion of the fourth D₂ molecule in the cage at ~130 K. Above 130 K two or three molecules are rotating inside the cage yielding an average uniform spherical distribution of the nuclear density.

At 2 kbar pressure incorporation of the fourth hydrogen molecule in the large cage is complete at ~180 K. At this temperature the D₂ molecules are almost delocalized and only a small localized fraction refined. That residual part of localized D₂ molecules may indicate that rotation of four D₂ molecules in the large cage is substantially restrained and their average distribution could not

be described as spherical with the same accuracy as for 2-3 molecules in the cage. Below 160 K the localized fraction increases, and at 40-50 K the D_2 molecules were found only in fixed positions.

Cooling of the clathrate evidences the domination of van der Waals forces over the thermal energy of the D_2 molecules, and their localization occurs in the temperature range 50-160 K. Assuming that the D_2 molecules are almost non-bonded above 160 K we can roughly estimate the maximum energy of thermal vibrations as $5/2 kT$, and accordingly, the interaction between a deuterium molecule and six framework oxygen atoms as 3.3 kJ/mol. Such interaction results in the strong attraction of D_2 electron density by oxygen atoms, decreasing the repulsion between D_2 neighboring molecules. This allows the formation of the tetrahedral cluster, which is stable under normal pressure with a D_2 - D_2 distance of 2.93 Å; this bond distance is much smaller than that in solid hydrogen at normal pressure (3.78 Å) [18].

CONCLUSIONS

A new experimental setup for neutron diffraction at high hydrostatic pressure (up to 10kbar) and in the 10-300 °K temperature range has been developed at the LANSCE/Lujan-Center at the Los Alamos National Laboratory. The crystal structure transformations of $H_2(D_2)$ clathrate were determined as a function of temperature and pressure. Hydrates of Ne, N_2 , Ar, Kr and Xe were extensively studied, as well. At ambient pressure multiple guests' occupancies in the cages were found for H_2 and Ne clathrates. Hydrogen occupancy in the $(32+X)H_2 \cdot 136H_2O$, $x=0-16$ clathrate varies by changing the large (hexakaidecahedral) cage occupancy between 2 and 4 molecules, but keeping single occupancy of the small (dodecahedral) cage in the sII structure. Distribution of the guest hydrogen molecules inside the cages depends on temperature and undergoes the localization-delocalization transition. At low temperature, the guest hydrogen molecules are localized; with increasing temperature they can more freely rotate yielding a nearly spherical density distribution inside the cages. Neon clathrate also crystallizes in the sII but has the fixed composition of $32Ne \cdot 136H_2O$ corresponding to singly occupied dodecahedral cage and double occupancy in the hexakaidecahedral cage. The guest-host interaction plays an important role in the clathrate structure formation and stability.

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